酸化鉄ナノ粒子を出発物質とした鉄基機能性材料創製とその磁気特性制御

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論文内容要約

Chapter 1　Introduction

Metallic α-Fe nanoparticle has long been of technological interest because of its large saturation magnetization (M_s : 218 emu/g) and the controllability of magnetic characteristic by particle size or shape. However, it is difficult to keep the condition of metallic α-Fe nanoparticles because α-Fe nanoparticles are easy to oxidize at the moment of exposure to air, and form iron oxides or hydroxides. In order to use metallic α-Fe nanoparticles for various applications such as MRI imaging, magnetic sensors, electromagnetic wave absorber or soft phase of nanocomposite magnets with high-density magnetic energy, the prevention of oxidation is indispensable.

ε-Fe_2O_3 nanoparticles have also received much attention due to their large coercivity (H_c > 20 kOe) at room temperature. However, it is very difficult to obtain single-phase ε-Fe_2O_3 nanoparticles, because ε-Fe_2O_3 phase is an intermediate phase on the transformation from γ-Fe_2O_3 phase to α-Fe_2O_3 phase. To prepare ε-Fe_2O_3 phase selectively, focusing on the formation energy of ε-Fe_2O_3 phase is important.

These two kinds of iron-based magnetic materials, α-Fe nanoparticles and ε-Fe_2O_3 nanoparticles, can be prepared by crystal structure transformation of size-controlled iron oxide nanoparticles followed by heat treatment. Therefore, the purpose of this study is the preparation of next-generation high performance iron-based magnetic materials from iron oxide nanoparticles as starting material. The objectives of each chapter are as follows.

Chapter 2: Synthesis of size-controlled iron oxide nanoparticle

SiO_2 coating of iron oxide nanoparticle surface to prevent particle aggregation during heat treatment

Chapter 3: Preparation of passivated α-Fe nanoparticles and their magnetic properties control

Chapter 4: Preparation of single-phase ε-Fe_2O_3 nanoparticles and investigation of their magnetic properties

Chapter 2 Synthesis of the SiO_2 coated Iron Oxide Nanoparticles

In this study, Iron oxide nanoparticles were synthesized by thermal decomposition of $Fe(acac)_3$ in the mixture of oleic acid and oleylamine as solvent and surfactant. In this method, the obtained particles can be stably dispersed in nonpolar solvent because the surface of nanoparticles are modified with alkyl chains. The typical synthesis procedure of iron oxide nanoparticles is as follows. First, the mixture of $Fe(acac)_3$, 1,2-Hexadecandiol, oleic acid and oleylamine was heated at 130 ºC under 100 Pa with vigorous stirring. After 30 min heating at this temperature, the solution was heated to 250 ºC by 10 ºC /min and reacted for 3 h. After the reaction, mantle heater was rapidly removed and cooled to room temperature. Figure 1(a) shows the TEM image of obtained nanoparticles under this condition. Sphere-shaped 8.2 nm nanoparticles were formed. The XRD measurement showed that the crystal structure was Fe_3O_4 (magnetite). On the other hand, cubic shaped monodisperse FeO (wüstite) nanoparticles were formed when 1,2-Hexadecandiol was not added in the system (Figure 1(b)～(d)). The final particle size can be controlled with preheating time at 210 ºC (16 h : 59.5 nm, 24 h : 40.9 nm, 32 h : 23.6 nm). Long preheating treatment resulted in the decrease of particle size, since large number of nuclei were formed by thermal decomposition of iron precursor. In this system, oleic acid was acted as shape controller. On the other hand, oleylamine was acted as reducing agent. The size-controlled monodisperse iron oxide nanoparticles were successfully synthesized by these methods.

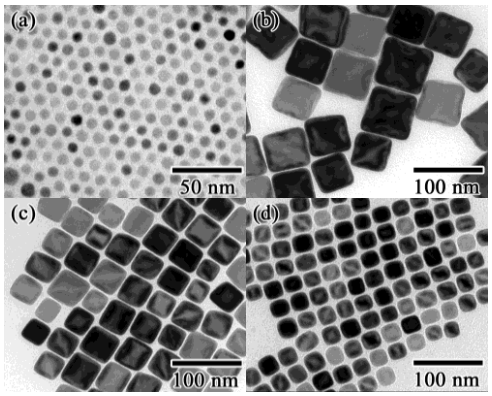

Figure 1: TEM images of synthesized iron oxide nanopartircles
(a): 8.2 nm Fe_3O_4
(b): 59.5 nm FeO (preheating 16 h)
(c): 40.9 nm FeO (preheating 24 h)
(d): 23.6 nm FeO (preheating 32 h)

The obtained iron oxide nanoparticles were coated with SiO_2 shell through the formation of water-in-cyclohexane reverse micro emulsion and hydrolysis of tetraethyl orthosilicate (TEOS), in order to prevent aggregation of iron oxide nanoparticles by heat treatment. Figrue 2 shows the TEM images of obtained SiO_2 coated iron oxide nanoparticles. Uniform SiO_2 shell was observed on the surface of each iron oxide nanoparticles. The formation of SiO_2 nanoparticles without iron oxide core were supressed by increasing the added amount of iron oxide nanoparticle in the solution. The XRF measurement indicated that the SiO_2 shell was formed in concurrence with initial Fe/Si value. The SiO_2 shell thickness can be precisely changed by the amount of TEOS.

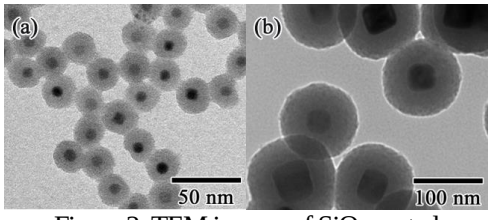

Figure 2: TEM images of SiO_2 coated iron oxide nanoparticles
(a): 8.2 nm Fe_3O_4@SiO_2
(b): 40.9 nm FeO @SiO_2

Chapter 3 Preparation of passivated α-Fe nanoparticles and their oxidation resistivity

The obtained SiO_2 coated Fe_3O_4 nanoparticles (Fe_3O_4 : 8.2 nm, SiO_2 shell thickness : 8.3 nm) were reduced to α-Fe@SiO_2 nanoparticles under 100%-H_2 atmosphere at 600 ºC, and then they were heated at 300-400 ºC under 2%-O_2/N_2 atmosphere to form the oxide layer on α-Fe particle surface. The TEM image of nanoparticles before and after heat treatment showed SiO_2 coated structure was kept and particle aggregation was prevented even after heat treatment under high temperature. Figure 3 shows the XRD patterns of the Fe_3O_4@SiO_2 nanoparticles before and after heat treatment. Fe_3O_4 phase was completely changed into metallic α-Fe phase by reduction treatment. At 300 ºC partial oxidization resulted in solely the observation of α-Fe peaks. On the other hand, the patterns not only α-Fe phase but also Fe_3O_4 phase were observed in the case of 400 ºC. These results show that the progress of oxidation can be easily controlled by heating temperature.

The oxidation resistivity of heat treated nanoparticles was investigated by measuring the change of M_s value with time under the air (Figure 4). In the case of the α-Fe nanoparticles without surface oxidization, M_s was decreased about 40% in 1 day. Judging from this result, SiO_2 shell on the outermost surface of nanoparticle has no oxidation resistivity due to their porous structure. The XRD pattern of re-oxidized nanoparticles showed that α-Fe nanoparticles were converted into low crystalline Fe_3O_4 nanoparticles. By contrast, in the case of the partially oxidized α-Fe nanoparticles, the decrease of M_s was not observed even after 80 days (300 ºC : -4.1%, 400 ºC : -3.7%). Moreover, the XRD patterns of partially oxidized α-Fe nanoparticles resulted in the observation of α-Fe phase after 80 days. These results show the oxide layer on metallic α-Fe nanoparticles maintains the condition of α-Fe phase. In addition to the stability under the air, the oxidation resistivity of obtained nanoparticles in the water was also investigated. It is noteworthy that the partially oxidized nanoparticles can keep their high M_s value over 1 week in the deionized water. Hence, the partial oxidation treatment under low O_2 atmosphere is so effective to protect α-Fe phase from oxidization in the air or water for long time. The effect of α-Fe particle size on magnetic property was investigated by using larger FeO nanoparticles as starting material. As a result of *M-T* curve measurement, it was found that the blocking temperature (T_b) of α-Fe nanoparticles gradually increases with the particle size. The magnetic state changed from superparamagnetism into ferromagnetism over 24 nm.

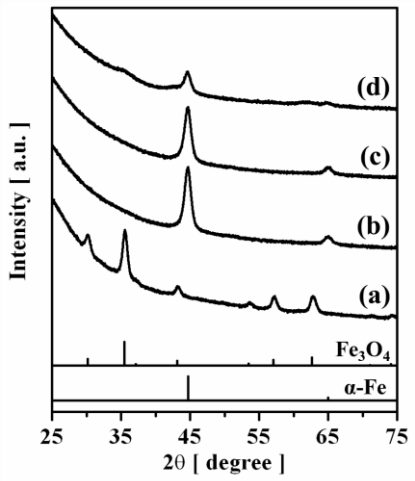

Figure 3: XRD patterns
(a) as-synthesized Fe_3O_4@SiO_2 nanoparticles
(b) after reduction treatment
(c) after partial oxidation at 300 °C
(d) after partial oxidation at 400 °C

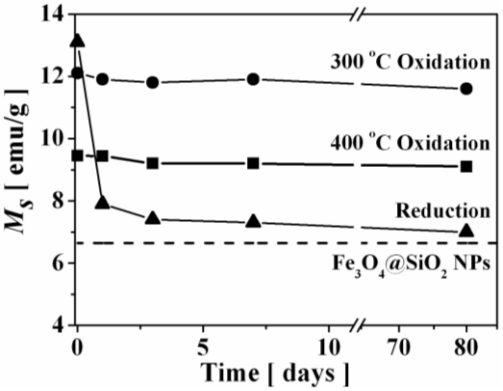

Figure 4: The dependence of M_s as a function of time.

Chapter 4 Preparation of ε-Fe_2O_3 nanoparticles and their magnetic properties

In this study, the effects of treatment temperature and particle size on the formation of ε-Fe_2O_3 phase were investigated. The obtained FeO@SiO_2 nanoparticles (FeO : 40.9 nm, Fe/Si molar ratio : 0.1) were sintered in the air by muffle furnace to transform into ε-Fe_2O_3 nanoparticles. Figure 5 shows the XRD patterns of nanoparticles sintered at 1000, 1100, 1200 ºC for 200 h. The patterns of 1000 ºC and 1200 ºC show the formation of γ-Fe_2O_3 and α-Fe_2O_3 phase respectively. On the other hand, 1100 ºC treatment resulted in the formation of orthorhombic ε-Fe_2O_3 phase. The crystalline sizes of each sample were calculated by Scherrer's equation. The crystalline sizes of all samples were close to the initial FeO nanoparticle size. In the case of Fe/Si value were 0.3, not only ε-Fe_2O_3 phase, but α-Fe_2O_3 phase were formed at 1100 ºC. This is more pronounced for the sample with Fe/Si = 0.5, which resulted in the observation of only α-Fe_2O_3 phase. The crystalline size of α-Fe_2O_3 phase was over 100 nm. These results indicated that particle aggregation was occurred during heat treatment. Therefore, thick SiO_2 shell (Fe/Si > 0.1) is needed to prevent aggregation of iron oxide nanoparticles during heat treatment under high temperature.

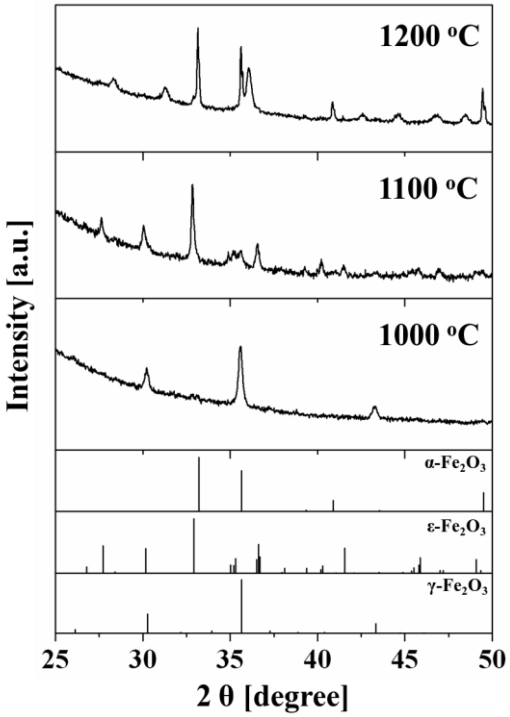

Figure 5: The XRD patterns of calcined nanoparticles at different temperatures.

Figure 6(a) shows the TEM image of nanoparticles sintered at 1100 ºC for 200 h. The significant aggregation of iron oxide nanoparticles was not observed. On the other hand, the SiO_2 shell on the particle surface was aggregated, which changed into SiO_2 matrix. These crystallized SiO_2 could be removed by alkaline treatment. Figure 6(b) shows the TEM image of nanoparticles after alkaline etching in the 8.0 mol/L NaOH aqueous solution at 80 °C for 24 h. The iron oxide nanoparticle size measured by this image was 41.0 nm. Judging from these results, it was found that the crystal structure transformation was occurred with keeping the initial iron oxide nanoparticle size by uniform and thick SiO_2 shell. FeO@SiO_2 nanoparticles were treated at 1100 °C for 5, 20, 100, 200 h to observe phase transformation behavior with heating time. After 5 h calcination, only γ-Fe_2O_3 phase was observed. By prolonging the heat treatment time, the content of ε-Fe_2O_3 phase was increased. Finally, the ε-Fe_2O_3 phase was observed as the major phase after 200 h annealing.

Figure 7 shows the *M-H* curve of obtained ε-Fe_2O_3 nanoparticles measured by superconducting quantum interface device (SQUID) at 300 K. Prepared nanoparticles showed single loop and hard magnetism with large coercivity value (23.4 kOe) at room temperature.

To investigate the effect of iron oxide nanoparticle's size on phase transformation behavior, FeO@SiO_2 nanorparticles with different FeO core size were treated under the same condition. The sizes of treated FeO nanoparticle were 23.6 ± 2.0 nm and 59.5 ± 8.2 nm. The Fe/Si value was fixed to 0.1. As a result, in the case of 23.6 nm FeO, the formation of ε-Fe_2O_3 phase was observed. However, γ-Fe_2O_3 phase was formed as main phase. The *M-H* curve also shows the existence of soft magnetic γ-Fe_2O_3 phase and hard magnetic ε-Fe_2O_3 phase. By contrast, only α-Fe_2O_3 phase was formed when 59.5 nm FeO nanoparticles were used as starting material. These results revealed that the particle size has a strong effect on phase transformation behavior and stability of each Fe_2O_3 polymorphs (γ-Fe_2O_3, ε-Fe_2O_3 and α-Fe_2O_3). Hence, the precise control of particle size is quite important for the synthesis of single phased ε-Fe_2O_3 nanoparticle.

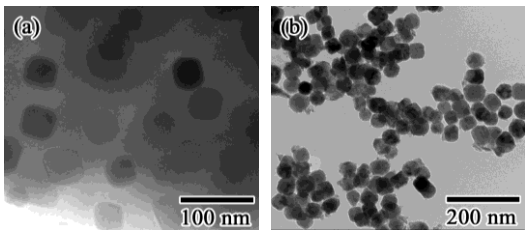

Figure 6: TEM images of
(a) calcined nanoparticles (1100 ℃, 200 h)
(b) after SiO_2 removal

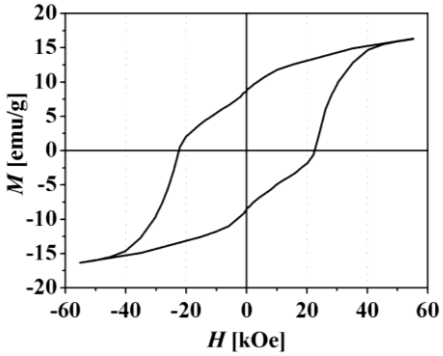

Figure 7: *M-H* curve of ε-Fe_2O_3 nanoparticles
(measured at 300 K)

Chapter 5 Summary

Uniform iron oxide (Fe_3O_4 and FeO) nanoparticles were synthesized by thermal decomposition method. Particle size can be controlled by the amount of reductant or pre-heating treatment time. The obtained iron oxide nanoparticles were coated with uniform SiO_2 shell by reverse micro micelle method. The SiO_2 shell thickness could be controlled by the amount of TEOS. The obtained particles were used for the starting material.

Passivated α-Fe nanoparticles were synthesized by partial oxidation treatment for α-Fe nanoparticles. The partial oxidation treatment under low O_2 atmosphere is so effective to protect α-Fe phase from oxidization in the air or water for long time. Moreover, the blocking temperature (T_b) of α-Fe nanoparticles can be controlled by the initial particle size. The magnetic state changed from superparamagnetism into ferromagnetism over 24 nm.

Single phased ε-Fe_2O_3 nanoparticles were successfully synthesized by heat treatment to the FeO nanoaprticles with SiO_2 shell. The crystal structure transformation was occurred with keeping the initial iron oxide nanoparticle size by uniform SiO_2 shell. Prepared ε-Fe_2O_3 nanoparticles showed hard magnetism with large coercivity value (23.4 kOe) at room temperature. It was found that the precise control of particle size is so important for the synthesis of single phased ε-Fe_2O_3 nanoparticle.